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Kakovost zraka na delovnem mestu - Vzorčenje in analiza hlapnih organskih spojin z desorpcijo s topilom in s plinsko kromatografijo - 1. del: Metoda vzorčenja s črpanjem

Workplace air quality - Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography - Part 1: Pumped sampling method

Qualité de l'air des lieux de travail - Échantillonnage et analyse des composés organiques volatils par désorption au solvant/chromatographie en phase gazeuse - Partie 1: Méthode d'échantillonnage par pompage

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Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography —

Part 1: Pumped sampling method

Qualité de l'air des lieux de travail — Échantillonnage et analyse des composés organiques volatils par désorption au solvant/chromatographie en phase gazeuse —

Partie 1: Méthode d'échantillonnage par pompage

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 16200 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 16200-1 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

ISO 16200 consists of the following parts, under the general title *Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography*:

— *Part 1: Pumped sampling method*

— *Part 2: Diffusive sampling method*

Annexes A, B and C of this part of ISO 16200 are for information only.

Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography —

Part 1: Pumped sampling method

1 Scope

This part of ISO 16200 gives general guidance for the sampling and analysis of volatile organic compounds (VOCs) in air by solvent desorption/gas chromatography using pumped sampling.

This part of ISO 16200 is applicable to a wide range of VOCs, including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. A number of sorbents are recommended for the sampling of these VOCs, each sorbent having a different range of applicability. However, activated coconut shell charcoal is frequently used. Very polar compounds may require derivatization; very low boiling compounds will only be partially retained by the sorbents and can only be estimated qualitatively. Semi-volatile compounds will be fully retained by the sorbents, but may only be partially recovered.

The upper limit of the useful range is set by the sorptive capacity of the sorbent used and by the linear dynamic range of the gas chromatograph column and detector or by the sample-splitting capability of the analytical instrumentation used. The lower limit of the useful range depends on the noise level of the detector and on blank levels of analyte and/or interfering artefacts on the sorbent tubes or in the desorption solvent. Artefacts are typically subnanogram for activated charcoal, but higher levels of aromatic hydrocarbons have been noted in some batches.

The concentration range for which this part of ISO 16200 is valid for the measurement of airborne vapours of VOCs is dependent on the volume sampled. For example, for a 10-litre sample of air, the range is approximately 1 mg/m^3 to 1000 mg/m^3 individual organic compound. For a 1-litre sample of air, the range is approximately 10 mg/m^3 to 10 000 mg/m^3 individual organic compound, and *pro rata*.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 16200. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 16200 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

EN 1232, *Workplace atmospheres — Pumps for personal sampling of chemical agents — Requirements and test methods*

EN 1540, *Workplace atmospheres — Terminology*

3 Principle

A measured volume of sample air is drawn through one (or more) sorbent tubes in series; an appropriate sorbent (or sorbents) being selected for the compound or mixture to be sampled. Provided suitable sorbents are chosen, volatile organic components are retained by the sorbent tube and thus are removed from the flowing air stream. The collected vapour is desorbed by a solvent, typically carbon disulfide, and the solution is analysed with a gas chromatograph equipped with a flame ionization detector, mass spectrometer or other selective detector.

4 Reagents and materials

During the analysis, use only reagents of analytical reagent grade.

4.1 Volatile organic compounds

A wide range of VOCs are required as reagents for calibration purposes.

4.2 Desorption solvent

The desorption or elution solvent, commonly carbon disulfide, should be of chromatographic quality. It shall be free from compounds co-eluting with the substances of interest. Tables 1 and 2 give recommended desorption solvents for particular vapours (see 7.5).

Where necessary (see Note 2), a desorption solvent modifier should be added at a sufficient concentration to result in a homogeneous solution in desorbed samples. Dimethylformamide may be suitable for this purpose.

NOTE 1 Carbon disulfide is normally recommended for the desorption of non-polar compounds from activated carbon. For polar compounds and mixtures of polar and non-polar compounds there is no ideal universal desorption solvent. Dichloromethane, methanol, higher alcohols, dimethylformamide and acetonitrile have been used as eluents, either singly or mixed with each other or carbon disulfide. OSHA methods 07 and 100 [1] and the NISOH methods 1301, 1400, 1401, 1402, 1403 for ketones and alcohols [2] give examples of suitable desorption solvents other than pure carbon disulfide.

NOTE 2 The use of carbon disulfide desorption solvent can result in problems when polar analytes are collected from humid atmospheres. Polar analytes may be soluble in a water phase which forms following desorption with carbon disulfide when sufficient water is collected with the sample.

4.3 Sorbents

4.3.1 Activated charcoal

Tubes prepacked by the manufacturer with preconditioned charcoal are available and do not require further conditioning. Alternatively, tubes may be prepared by the user. A particle size of 0,35 mm to 0,85 mm is recommended. Before packing the tubes, the charcoal shall be heated in an inert atmosphere, e.g. high-purity nitrogen, at approximately 600 °C for 1 h. To prevent recontamination of the charcoal, it shall be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes.

The sorptive capacity and desorption efficiency of different batches of activated charcoal may vary. Commercial tubes, if used, should be purchased from the same batch and in sufficient number to provide consistent performance for a definite period of time.

NOTE Activated charcoal is usually processed from coconut shells. For some applications, petroleum-based charcoal is preferred (see Tables 1 and 2). Some manufacturers recommend synthetic carbons as alternatives to charcoal of biological origin.

4.3.2 Other sorbents

Sorbents other than charcoal may be used for certain applications (see Tables 1 and 2).

NOTE A description of sorbent types is given in annex A. Equivalent sorbents may be used.

4.4 Calibration standards

Calibration blend solutions are required in order to compare the concentrations of desorbed solutions (7.3) with those calibration standards in the gas chromatographic analysis. Such solutions should be prepared in a way that is traceable to national standards.

An internal standard is optional. If used, it should not interfere with the compounds of interest and it should not be removed from the elution solvent by the sorbent. In the context of this method, the purpose of the internal standard is to correct for small variations in the injection volume. The use of an internal standard as a surrogate to correct for desorption efficiency (e.g. *n*-propyl acetate in the analysis of *n*-butyl acetate) is not recommended. Desorption efficiency should be determined directly with the compounds of interest (7.5).

Storage times for calibration solutions vary according to application. Typically, carbon disulfide dilutions should be prepared fresh weekly, or more frequently if evidence is noted of decomposition or evaporation.

NOTE In the analysis of complex mixtures, calibration blends of the pure compounds may be prepared before dilution with the elution solvent. Examples of three calibration blends are listed here. These have been used in the analysis of mixed solvents in paints, thinners, adhesives, cleaning fluids and miscellaneous commercial products. The components are arranged to give resolved peaks on both BP-1 and BP-10 phases[1)]. Other blends may be more appropriate on different columns or in other applications. In the examples below, calibration blends 1-3 are stable for at least one year when stored in dark glass bottles with PTFE-lined screw-caps at less than 4 °C.

a) Blend 1 consists of: *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-undecane, *n*-dodecane, benzene, toluene, *o*-xylene, *p*-xylene, *n*-propylbenzene, isopropylbenzene, *o*-ethyltoluene, *m*-ethyltoluene, *p*-ethyltoluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, *n*-propyl acetate, *n*-butyl acetate, isobutyl acetate, butoxyethyl acetate.

b) Blend 2 consists of: isopropanol, isobutanol, *n*-butanol, 1-methoxy-2-propanol, butoxyethanol, toluene, ethylbenzene, 1,2,3-trimethylbenzene, ethyl acetate, ethoxyethyl acetate.

c) Blend 3 consists of: acetone, 2-butanone, 4-methylpentan-2-one, cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, isopropyl acetate, *n*-nonane, toluene.

4.4.1 Solution containing approximately 10 mg/ml of each liquid component

Weigh 1 g of the substance or substances of interest into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with desorption solvent (4.2), stopper and shake to mix.

4.4.2 Solutions containing approximately 1 mg/ml of liquid components

Introduce 50 ml of desorption solvent into a 100 ml volumetric flask. Add 10 ml of solution 4.4.1 Make up to 100 ml with desorption solvent, stopper and shake to mix.

4.4.3 Solution containing approximately 100 µg/ml of each liquid component.

Weigh 10 mg of the substance or substances of interest into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with desorption solvent (4.2), stopper and shake to mix.

4.4.4 Solution containing approximately 10 µg/ml of liquid components

Introduce 50 ml of desorption solvent into a 100 ml volumetric flask. Add 10 ml of solution 4.4.3. Make up to 100 ml with desorption solvent, stopper and shake to mix.

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1) BP-1 and BP-10 are examples of suitable products available commercially. This information is given for the convenience of users of this part of ISO 16200 and does not constitute endorsement by ISO of these products. Equivalent products may be used if they can be shown to lead to the same results. Annex B gives a non-exclusive list of products that are believed to be equivalent.

4.4.5 Solution containing approximately 1 mg/ml of gas components

For gases, e.g. ethylene oxide, a high-level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a precision 1-ml gas-tight syringe (5.8) with 1 ml of the pure gas and close the valve of the syringe. Using a septum vial of suitable capacity, add 2 ml desorption solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the desorption solvent. Open the valve and withdraw the plunger slightly to allow the desorption solvent to enter the syringe. The action of the gas dissolving in the desorption solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP occupies 22,4 litres.

4.4.6 Solution containing approximately 10 µg/ml of gas components

For gases, e.g. ethylene oxide, a low-level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic (or other inert material) gas bag from a gas cylinder. Fill a precision 10-µl gas-tight syringe (5.8) with 10 µl of the pure gas and close the valve of the syringe. Using a septum vial of suitable capacity, add 2 ml desorption solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the desorption solvent. Open the valve and withdraw the plunger slightly to allow the desorption solvent to enter the syringe. The action of the gas dissolving in the desorption solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP occupies 22,4 litres.

4.5 Calibration blend atmosphere (for 4.6 and annex B)

Prepare standard atmospheres of known concentrations of the compound(s) of interest by a recognized method. Methods described in ISO 6141, ISO 6145 and ISO 6349 are suitable. If the procedure is not applied under conditions that allow the establishment of full traceability of the generated concentrations to primary standards, confirm the delivered concentrations using an independent procedure.

4.6 Standards for desorption efficiency (for 7.5)

Prepare loaded sorbent tubes by passing an accurately known volume of the standard atmosphere through the sorbent tube, e.g. by means of a pump or mass flow controller. The volume of atmosphere sampled shall not exceed the breakthrough volume of the analyte-sorbent combination (annex B). After loading, the tube is disconnected and sealed.

If the generation of standard atmospheres is not practicable, the standards may be prepared by a liquid spiking procedure, provided that the accuracy of the spiking technique is established by using procedures giving spiking levels traceable to primary standards of mass and/or volume, or is confirmed by an independent procedure.

Load the sorbent tubes by injecting aliquots of standard solutions (4.4) of accurately known mass or volume onto clean sorbent tubes as follows: a sorbent tube is fitted to a T-piece of which one end is fitted with a septum, or injection facility of a gas chromatograph, through which inert purge gas is passed at 100 ml/min. Inject a 1 µl to 4 µl aliquot through the septum and purge for 5 min. Disconnect the tube and seal.

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 Sorbent tube

A sampling tube, typically consisting of a glass tube with both ends flame-sealed, 70 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm, containing two sections of sorbent. In the case of charcoal, the sorbing section contains 100 mg of charcoal and the back-up section, 50 mg. The sections are separated and their contents are held in place with an inert material, e.g. glass wool plugs (preferably silanized).

Glass tubes shall be held in protective holders to prevent breakage.

The desorption efficiency (D) for each batch of tubes shall be checked by one of the methods described in 4.6. If D is lower than 0,75 (75 %), the tubes shall not be used (but see below).

Tubes meeting these requirements are commercially available; however, they may also be made by the user. Metal tubes may also be used with appropriate end caps. Self-packed samplers should not be used unless they can be shown to have reproducible and constant sorption properties.

Where mixtures of non-polar analytes are desorbed with pure carbon disulfide, the mutual concentration effect on D is generally negligible. If the composition of a mixture of polar and non-polar analytes is known approximately, D values should be established with a similar mixture. It may not be possible to achieve greater than 75 % D for all components of such a mixture with a single desorption solvent. Provided that it can be established that the D is consistent and that no better solvent has been found, then a compromise is acceptable, although where possible, the taking of a second sample and optimizing desorption conditions for both polar and non-polar analytes is preferred.

NOTE 1 Instead of commercial two-section tubes, two single section tubes in series may be used. This arrangement has the advantage that it is not necessary to store tubes at subambient temperatures after sampling, to prevent migration of the sorbed compounds from one section to the other.

NOTE 2 Polyurethane plugs may be used in place of silanized glass wool; however, they are known to sorb certain pesticides [3] for which this part of ISO 16200 is inapplicable.

NOTE 3 When it is desirable to sample highly volatile compounds for extended periods, or at a high volume flowrate, a larger sampling device may be used, provided the proportions of the tube and its charcoal contents are scaled similarly to the base dimensions, to provide nominally the same linear flowrate and contact time with the charcoal bed.

5.2 End caps, made to fit snugly over the sorbent tubes (5.1) to prevent leakage or contamination and made of inert material such as polyethylene.

5.3 Sampling pump, fulfilling the requirements of EN 1232 or equivalent.

The sampling pump should be in accordance with local safety regulations.

5.4 Tubing, plastic or rubber, about 90 cm long of appropriate diameter to ensure a leak-proof fit to both pump and sample tube or tube holder, if used. Clips shall be provided to hold the sorbent tube and connecting tubing to the wearer's lapel area.

It is not recommended to use tubes with any tubing upstream of the sorbent, as sample losses may occur.

5.5 Gas chromatograph, fitted with a flame ionization, photo-ionization detector, mass spectrometric or other suitable detector, capable of detecting an injection of 0,5 ng toluene with a signal-to-noise ratio of at least 5 to 1.

A gas chromatograph column capable of separating the analytes of interest from other components. Examples of suitable choices are 50 m × 0,22 mm fused silica columns with BP-1 or BP-10 stationary phase. A typical film thickness is in the range 0,5 µm to 2,0 µm. Typical operating conditions for these columns might be temperature programming from 50 °C to 200 °C at 5 °C/min with a helium carrier gas flowrate of 0,7-0,8 ml/min. Annex B gives a list of equivalent phases.

5.6 Autosampler

These are commercially available with liquid-chilled sample trays, suitable for the analysis of volatile solvents.

5.7 Precision volumetric flasks, of accurately known volumes, to be used for the preparation of calibration blend solutions (4.4).

5.8 Precision gas-tight syringes, of accurately known volumes of 1,0 ml and 10 µl, readable to 0,1 ml and 1,0 µl, respectively.

5.9 Flow meter, soap bubble type, or other suitable device for calibrating the flowrate of sampling pumps. The flow meter readout should be traceably calibrated or checked to a primary flow standard.

NOTE The use of uncalibrated rotameter readouts for the calibration of pump flowrates may result in systematic errors of several tens of percent.

6 Sampling

6.1 Calibration of pump

Adjust the flowrate with a representative sorbent tube assembly in line, such that the recommended sample volume will be taken in the available time, using the internal meter. The flowrate should not exceed 200 ml/min (see annex C and EN 1076). The sample volume shall be less than the breakthrough volume (6.2, annex C). Calibrate the pump using an appropriate external calibrated meter (5.9). One end of the calibrated flow meter should be at atmospheric pressure to ensure proper operation. Additional information about pump calibration is given in [4].

6.2 General

Select a sampler appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in annex A. Published methods that give further information on sampling and analysis details for specific VOCs are referenced in Tables 2 and 3. The source references give details of suitable flowrates and recommended sampling times for particular VOCs. For most VOCs, a sample volume of at least 10 litres can be taken without breakthrough occurring on a standard-sized tube (5.1). For some more volatile VOCs, the safe sampling volume may be much less than this, and a standard tube may not have the capacity to sample for a full 8 h. An 8-h time-weighted average concentration can be derived from the results of two or more consecutive samples, or a larger sample tube may be used.

Break open both ends of the sample tube, ensuring that each opening is at least one half the inside diameter of the tube. Insert the tube into its protective holder and attach to the sampling pump (switched off) with the connecting tubing such that the back-up (50 mg) section is nearest the pump.

When used for personal sampling, mount the sampler in the breathing zone (as defined in EN 1540). When used for fixed location sampling, choose a suitable sampling site. In either case, the sampler should be mounted in a vertical position to minimize channelling of air through the sorbent sections.

Turn the pump on at the start of sampling. Record the time and the flowrate, or register reading if appropriate, when the pump was turned on. At the end of the sampling period, record the time and flowrate, or register reading, and turn the pump off. Normally, the sampled volume is calculated from the mean value of the initial and final flowrates, multiplied by the elapsed time, or from the register reading for a pump with automatic flow control, multiplied by the stroke volume. However, if the difference between the initial and final flowrates is greater than 10 %, the sample should be discarded.

Disconnect the sample tube assembly and seal both ends of each tube with end caps (5.2). Tighten these seals securely. The tubes should be uniquely labelled, e.g. by engraving. Solvent-containing paints and markers or adhesive labels should not be used to label the tubes.

Record air temperature and barometric pressure periodically during sampling if it is desired either to express concentrations reduced to specific conditions (8.1, Note) or to express concentrations in volume fractions (8.2).

NOTE 1 The sampling efficiency will be 100 %, provided that the sampling capacity of the sorbent has not been exceeded. If this capacity is exceeded, breakthrough of vapour from the front section to the back-up section will occur. The source references in Tables 1 and 2 give indicative values for breakthrough volumes for single components. The breakthrough volume is defined and may be determined as specified in annex C.

NOTE 2 The breakthrough volume varies with ambient air temperature, relative humidity, concentration of sampled vapour and of other contaminants, and with the sampling flowrate. An increase in any of these parameters causes a reduction in the breakthrough volume. The back-up section may be used as a check on breakthrough under practical conditions. Alternatively, two or more tubes can be run in parallel using different sample volumes (“distributed sample volumes”).

Field blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the samples except for the actual period of sampling. Label these as blanks.